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Introduction

Accurate information about water quality trends in agricultural watersheds is needed to inform agricultural policy and quantify the effectiveness of field and landscape management practices. Several studies predicted the increased conversion of soybean and pasture acres to more corn acres driven by corn ethanol production would increase N losses and river nitrate-nitrogen (NO_3-N) levels (Donner and Kucharik, 2008, Secchi et al., 2011, and Yang et al. 2012).

The Raccoon River Watershed (RRWS) is an important source for municipal drinking water supply, and land use within its basin is overwhelmingly agricultural (Schilling and Zhang 2004; Hatfield et al. 2009; Jones and Schilling 2011, 2013) Its water has some of the highest nitrate concentrations of the Mississippi River's 42 largest tributaries (Goolsby et al. 2000). Nitrate loss from the Raccoon and other similar streams links to Gulf of Mexico hypoxia (David et al. 2010). The Des Moines Water Works (DMWW), which provides drinking water to 500,000 people, operates an ion exchange nitrate removal plant to meet safe drinking water standards.

Crop production in the Raccoon basin increased steadily from 1960 until 1980. Approximately 80% of the watershed has been cropped with corn (*Zea mays* L.) and soybean (*Glycine max* [L.] Merr.) since 1980 (Jones and Schilling 2011). The environmental consequences of this have been recognized by the agricultural community. Nitrate loss is in this region, however, is strongly tied to river discharge and precipitation (Sprague et al. 2011). This weather-driven variability makes assessing progress toward water quality goals difficult.

Demonstrating and quantifying conservation effectiveness of NO_3-N reduction practices, even at the field scale, is very challenging (Mulla et al. 2008; Tomer and Locke 2011; Schilling et al. 2013). Credible data and sound analyses are needed so policy-makers can deliver limited public resources to where they can best be used for improving water quality in the Raccoon and other watersheds.

Our objective was to evaluate both water quality and nitrogen (N) input data provided by farmers to test the hypothesis that increased corn area in the RRWS impacts river NO_3-N levels.

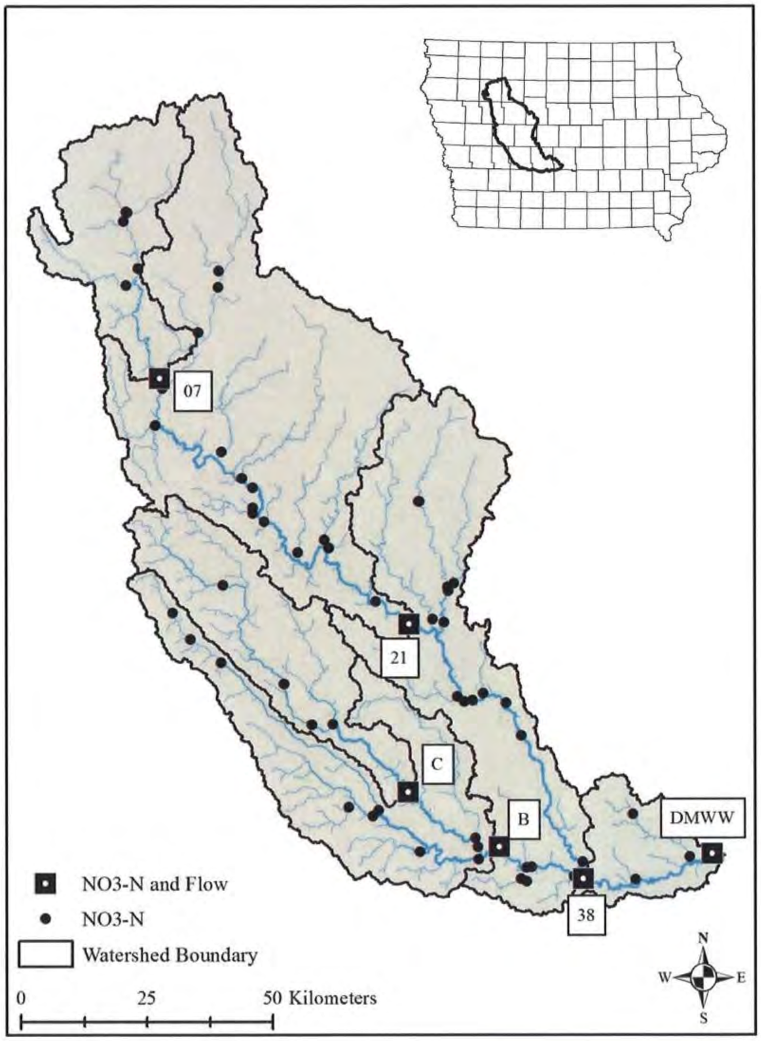

Figure 1. Location of Raccoon River watershed and water sampling locations.

Materials and methods

Raccoon River watershed

The Raccoon River drains an area of 2.3 million acres above the City of Des Moines in west-central Iowa (Figure 1). The Raccoon is really three rivers: the North, Middle and South Raccoon rivers are the major tributaries. The North Raccoon River drains the recently glaciated Des Moines Lobe landform, which features low relief and poor surface drainage (Prior, 1991). Greater than 50% of the agricultural land area in this region of Iowa has tile drainage (Schilling et al. 2008). The South Raccoon River drains an older pre-Illinoian glacial landscape (Southern Iowa Drift Plain) that is hillier with better-developed natural drainage. The Middle Raccoon River drains both of these landforms.

Water quality data

Water quality samples from near the mouth of the river were collected and analyzed by the Des Moines Water Works (DMWW) laboratory. Nitrate was measured in 3037 samples for the period January 1, 1999 through July 31, 2014. Samples sponsored by Agriculture's Clean Water Alliance (ACWA) were collected by a network of volunteers coordinated by the Iowa Soybean Association. This monitoring program follows a Quality Assurance Project Plan approved by Iowa DNR. Samplers are certified in proper sample collection techniques using IOWATER Volunteer Water Monitoring Program protocols (Iowa Department of Natural Resources, 2014). The ACWA monitoring plan varies some from year to year, depending upon the number of volunteers, past data, weather, or budget. These samples usually were collected every other Thursday, April through July, when 66% of the N load is transported by the river. A total of 64 sites in the RRWS were monitored for NO_3-N at least 30 times since 1999, and a total of 6842 samples were collected and analyzed.

Nitrate-N loads and yields (April-July) were assessed at five ACWA sites located near USGS flow gauges (Site 07-Sac City, Site 21-Jefferson, Site C-Panora, Site B-Redfield, and Site 38-Van Meter) (Figure 1) (USGS 2014). Average daily loads for each month (April-July) were calculated using linear interpolation methods. Interpolated daily concentrations were multiplied by corresponding daily discharges to obtain daily NO_3-N loads. Total values for April-July were calculated by summing monthly values. January-December loads for the DMWW location were calculated similarly. Discharge at the DMWW site was calculated by summing the discharge from Van Meter and Walnut Creek, a tributary that enters the Raccoon between Van Meter and DMWW.

Nitrate-N concentration data were tested for seasonal trends using the ESTREND software developed by USGS (Schertz et al. 1991, Helsel et al. 2006). The Seasonal Kendall test determines whether there is monotonic (single-direction) trend over time. Concentration trends were determined at the 41 tributary sites (5620 samples) and the site near the mouth at DMWW where sufficient data points existed (Schertz et al., 1991). At the six sites where discharge data were available (five ACWA sites and DMWW), flow-adjusted concentration trends were also calculated. Flow adjusted concentrations describe the relationship between flow and concentration prior to testing for trend. Load trends were determined at the six sites after the effect of precipitation had been removed by linear regression.

Weather data

We obtained monthly precipitation and temperature data from four stations in the Raccoon basin: Storm Lake, Rockwell City, Guthrie Center, and Des Moines (Iowa State University 2014). These stations are respectively located in the northwest, northeast, southwest, and southeast sections of the watershed. Watershed precipitation and temperature values were estimated by averaging data from the four locations.

Field management data and nitrogen budget

This study used actual management data collected from farmers who participated in Iowa Soybean Association's On-Farm Network statewide agronomic studies from 2006-2013 (Kyveryga et al. 2010, 2011; On Farm Network, 2014). Farmers, crop consultants and agronomists used the corn stalk nitrate test and late season aerial imagery for their fields to identify management, soil, and weather factors that impacted corn nitrogen status within fields. The management information included previous crop, timing of fertilizer and animal manure application, form of N applied, total applied N rates, and tillage type. Included within this data set was a subset of 698 fields in the 17 counties of the RRWS, with a minimum of 3 fields in each county. The area total of these fields was 55900 ac, about 1.2% of the cropped acres in the counties of the watershed. Figure 2 illustrates locations of these fields in the watershed.

To determine corn and soybean area in the RRWS for 1998-2013, the crop areas for each county were obtained (USDA 2014) and then adjusted according to the portion of the county within the watershed. From the crop area data we calculated the corn following corn and corn following soybean areas for each year.

The On-Farm Network N-rate data (Kyveryga et al. 2010, 2011; On Farm Network, 2014) includes N rate to each corn rotation (corn following corn and corn following soybean) and the type of N input (commercial or manure) for each field. Average N rates for the four corn categories (corn-corn-manure, corn-corn-commercial, corn-soybean-manure, and corn-soybean-commercial) were calculated from the On-Farm dataset (table 3). We then used these averages to calculate the total N applied to corn in the watershed 1999-2013, assuming the portion of watershed area receiving commercial versus manure N was the same as that in the On Farm Network dataset and that the 2006-2013 fertilization data was valid for the water quality period of record (1999-2014). We believe it is because N rate trends were not apparent in the On-Farm data, and previous research (Hatfield et al. 2009) showed no trend for the 15 years prior to 2003.

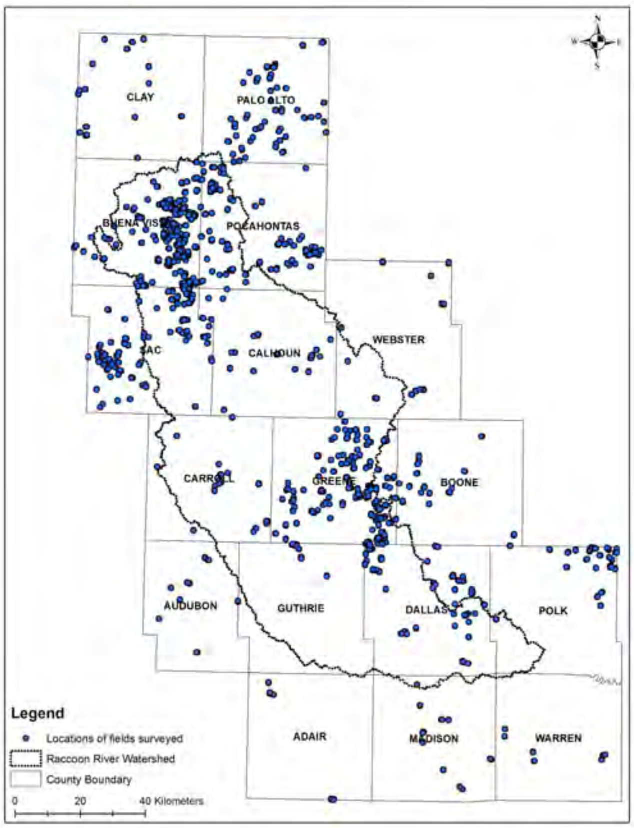

Figure 2. Location of corn fields by Iowa Soybean Association On-Farm Network. Nitrogen management data and rates were used in N balance calculations.

We used a statewide average N rate to soybean of 14 lb N/ac (USDA 2014). County-level crop yield data were also obtained from the National Agricultural Statistics Service (USDA, 2014), and then adjusted for moisture (Adviento-Borbe et al. 2007) and to the portion of each county within the watershed.

Biological N fixation of soybean in the previous year was calculated according to Barry et al. (1993) using Eq. 1:

$$\text{N fixed (lbs/ac)} = 33.4 \times \text{soybean yield (tons/ac)} - 110.7 \qquad [2]$$

Nitrogen additions with precipitation were calculated by averaging annual precipitation from the four watershed stations and multiplying by the 1.5 mg L^{-1} (ppm) measured by Hatfield et al. (1996) for central Iowa. Precipitation also was used to calculate dry deposition amounts (Goolsby et al. 1999). Total inputs were then calculated by summing N with fertilizer (manure and commercial), biological fixation, precipitation and deposition.

Export of N in corn grain was calculated using the measured two-year average reported by Blesh and Drinkwater (2013) for GMO varieties of this crop (1.2% N) in the US Midwest. Export of N in soybean was calculated assuming 6.4% N in soybean seeds (USDA 2009). We then used input data and January-December DMWW NO_3-N load data to construct a simplified N budget.

We acknowledge other minor N flow pathways exist; however, we focused on N budget components that could be linked to measurements made during the study. Clearly N pathways in larger watersheds such as the RRWS are more diverse; however, since N point sources and other urban contributions are relatively small (6%) in the sparsely-populated RRWS (Schilling et al. 2008) and agriculture dominates land use, we concluded that focusing on these major N flow paths was sufficient to meet our study objectives. Nitrogen returned to the soil from the previous year's crop residue was calculated according to Christianson et al. (2013) and Helmers and Castellano (2015).

Results

Weather

Annual RRWS precipitation for 1999-2013 averaged 33.1 inches, 2.1 above the 1893-2013 average, and ranged from 22.5 in 2012 to 46.3 in 2007. The 1999-2013 period was marked by extremes, as 2007-2010 was the wettest 4-year period since 1893, whereas 2012 and 2000 were the 10th and 15th driest years, respectively, since 1893. The April-July period, when the ACWA water monitoring was conducted, was consistent with annual patterns.

Nitrate concentrations, loads and yields

Average April-July NO3-N concentrations for the ACWA sites (Figure 1) ranged from 2.3 to 28.0 ppm. Average April-July concentrations exceeded 10 ppm at 75% of the sites. Nearly all (49/50) of the ACWA sites monitored in 2013 had their highest NO_3-N concentration in that year. The highest sample measured was 68 ppm at Site-14 Elk Run Creek in 2013. The average concentration across all sites averaged 18 ppm in 2013 compared to 6.4 ppm in 2000. Of the sites where sufficient continuous data existed to conduct trend analyses (Table 1), highest April-July concentrations were found in Elk Run Creek and Outlet Creek in the western portion of the RRWS where average concentrations measured during the April-July period were 19.5 and 23.1 ppm, respectively.

Table 1. April-July NO_3-N concentrations (ppm) of trended ACWA-RRWS sample sites, 1999-2014

Site	Description	Latitude (N)	Longitude (W)	Average NO_3-N ppm†	n‡	1999-2014 trend§ (ppm/yr)
01	Lateral 2	42°43′10″	95°4′21″	14.0	67	-0.23
02	N Raccoon R	42°43′11″	95°4′32″	12.2	83	-0.29
03	Poor Farm Cr	42°42′10″	95°4′55″	12.6	109	-0.43
04	Little Cedar C	42°37′4″	94°50′49″	12.6	110	-0.16
06	Prairie Cr	42°30′21″	94°53′41″	12.4	122	-0.20
08	Cedar Cr	42°24′14″	94°58′40″	12.6	126	-0.30*
05	Outlet Cr	42°35′13″	95°4′19″	23.1	153	-1.16*
07	N Raccoon R	42°25′19″	94°59′5″	13.1	129	-0.37**
09	Indian Cr	42°20′13″	94°59′38″	8.5	131	-0.23
10	Camp Cr	42°17′31″	94°49′55″	12.6	119	-0.51
11	Prairie Cr	42°30′21″	94°53′42″	13.3	115	-0.35
12	Lake Cr	42°14′42″	94°46′55″	11.2	120	-0.24
13	N Raccoon R	42°13′44″	94°45′22″	11.9	126	-0.24
14	Elk Run Cr	42°11′31″	94°45′18″	19.5	152	-0.32
17	Cedar Cr	42°8′13.2″	94°34′52″	13.0	121	-0.21
19	Purgatory Cr	42°6′50″	94°38′38″	12.4	121	-0.31
16	W Buttrick Cr	42°12′33″	94°21′20″	15.6	164	-0.65**
20	E Buttrick Cr	42°2′60″	94°16′52″	12.6	169	-0.59**
23	Buttrick Cr	41°59′35″	94°17′28″	13.5	138	-0.55*
21	N Raccoon R	42°1′44″	94°27′22″	11.6	173	-0.24
22	Hardin Cr	41°59′53″	94°19′8″	13.1	140	-0.43*
24	Greenbrier Cr	41°51′36″	94°15′22″	12.3	131	-0.32
A	N Raccoon R	41°33′54″	93°57′11″	11.1	193	-0.43**
44	M Raccoon R	42°3′11″	94°49′23″	11.1	158	-0.22
26	M Raccoon R	41°48′18″	94°36′11″	12.8	127	-0.02
25	Willow Cr	41°48′22″	94°33′14″	11.9	127	0.06
C	M Raccoon R	41°41′13″	94°22′19″	8.5	193	-0.18
30	Mosquito Cr	41°36′22″	94°12′36″	12.1	126	-0.20
31	M Raccoon R	41°35′24″	94°12′11″	8.8	152	-0.09
42B	Brushy Cr	42°0′4″	94°56′28″	16.0	99	-0.06
42A	Brushy Cr	41°57′14″	94°53′53″	14.3	131	-0.15
43	Brushy Cr	41°54′47″	94°49′19″	12.5	195	-0.25
28	Brushy Cr	41°39′7″	94°26′28″	8.5	134	-0.07
28A	S Raccoon R	41°38′35″	94°27′14″	5.1	117	-0.01
32	S Raccoon R	41°34′1″	94°12′4″	5.6	161	0.02
B	S Raccoon R	41°35′24″	94°9′4″	7.7	183	-1.65
33	Panther Cr	41°33′14″	94°5′10″	13.5	137	-0.17
37	S Raccoon R	41°32′17″	93°58′26″	7.8	165	-0.06
38	Raccoon R	41°32′2″	93°57′ 0″	9.3	157	-0.20
70	Walnut Cr	41°39′7″	93°50′2″	11.3	108	-0.23
40	Walnut Cr	41°34′33″	93°41′46″	7.0	138	-0.29
DMWW	Fleur	41°34′54″	93°38′34″	9.6	1322	-0.33*

†Calculated by averaging the yearly April-July averages.
‡Number of samples collected 1999-2014
*p< 0.10
**p< 0.05

Despite exceptionally high concentrations measured in 2013, the 1999-2014 concentration showed 39 of the 41 sites had decreasing trends. The average trend was minus 0.265 ppm/yr. Eight sites had statistically significant negative trends at $p<0.10$ and four sites at $p<0.05$. All sites with $p<0.10$ were in the North Raccoon Watershed, which drains the Des Moines Lobe landform exclusively. The probability of 39 out of 41 sites declining randomly was <0.001%.

The April-July trend measured at the mouth (DMWW site) was minus 0.33 ppm/yr ($p=0.098$), while the January-December trend was minus 0.13 ppm/yr ($p=0.15$).

Similar to concentrations, NO_3-N loads were highly variable. Average April-July loads ranged from 1377 tons at Site C-Panora to 14353 tons at Site 38-Van Meter with loads increasing downstream (data not shown). Years with the largest loads varied among sites, as the post-drought year of 2013 was the highest loading year only for Site 38-Van Meter, whereas at other sites, the largest April-July loads occurred in 1999 (Site 21-Jefferson), 2007 (Site B-Redfield) and 2009 (Site 7-Sac City and Site C-Panora). Loads measured during the April-July period at these five sites were significantly correlated with April-July precipitation ($r=0.79$). We evaluated precipitation-corrected loading trends for each of these five sites. This was done using a simple linear regression of April-July precipitation versus river load. While all five showed a modest decline, only the Jefferson site exhibited a statistically significant change ($p<0.05$).

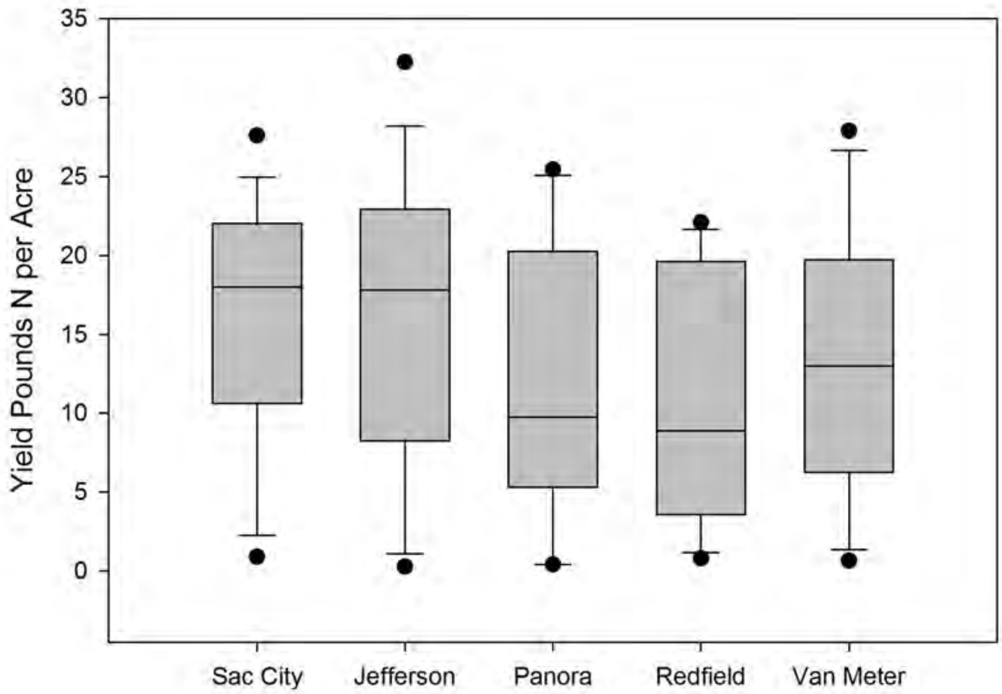

Figure 3. April-July NO3-N yields at the five flow-gauged ACWA sites, 1999-2014. The box represents the middle 50% of years, the black line the median and the whiskers the minimum and maximum.

April-July N yield from the five flow-gauged ACWA sites is shown in Figure 3. The two sites on the tile-flow-dominated (Des Moines Lobe) North Raccoon River, Site 07-Sac City and Site 21-Jefferson, had the highest average yields 15.9 lbs cropped/ac. These two sites also have the highest percentage of land in row crop (85.4 and 83.4%, respectively). Overall, the RRWS (at Van Meter) had an average April-July NO_3-N yield of 13.3 lbs/cropped-ac for the 16-year water monitoring period, ranging from 0.65 lbs/cropped-ac in 2000 (dry year) to 27.9 lbs/cropped-ac during the wet year of 2013.

Trends in crop area, nitrogen fertilizer usage, and tillage

Watershed area planted to corn steadily increased during the study period ranging from a low from 897000 ac (38.7% of RRWS area) in 2001 to 1065000 ac in 2012 (45.9% of RRWS area) (figure 4). The increase in corn area was largely at the expense of soybean area which decreased from 882000 ac (38.0% of RRWS area) in 2001 to 672000 ac in 2012 (29.0% of RRWS area). Total crop area declined 2.5% during the study period, although most of this decline occurred in two increments from 2001 to 2002 and 2012 to 2013. The second decline is likely related to crop area that went unplanted during the historically wet spring of 2013. From 2002 to 2012, total cropped area averaged 1741000 ac with a range of 1725000 ac in 2006 to 1747000 ac in 2003.

Using the 2006-2013 On-Farm Network fertilization data, commercial and manure N rates applied by farmers to SB-C were 159 and 195 lbs/ac, respectively, while N rates applied to C-C were 189 lbs/ac for commercial N and 238 lbs/ac using manure N. A total of 38% of soybean fields, 2% of corn following corn fields, and 10% of corn following soybeans were No-Till, with no apparent trends toward or away from the practice.

Nitrogen Budget

A simplified N budget (Table 2) using major N sources and outputs was constructed to identify possible factors that contribute to water quality trends. The DMWW data (January-December) were used to calculate river NO_3-N load. Total inputs (fertilizer, precipitation/deposition, and biological fixation) averaged 193 lbs/ cropped/ac-yr, while measured outputs, corrected for point source loads (Schilling et al., 2008), 138 lbs/cropped-ac-yr. The difference between inputs and outputs ranged from 28.8 lbs/ cropped-ac in 2004 to 128 lbs cropped/ac in 2012, when a large excess was amassed because of drought-induced crop yield reductions and reduced river transport. For 1999-2013, river NO_3-N loss (after subtracting point sources) was 10.4% of total N inputs.

Table 2. On Farm Network fertilization rates reported by farmers, 2006-2013 in counties of the RRWS

	Commercial N				Manure N			
	Following soybean		Following Corn		Following Soybean		Following Corn	
year	Fields	Average Rate (lb/ac)	Fields	Average Rate (lb/ac)	Fields	Average Rate (lb/ ac)	Fields	Average Rate (lb/ ac)
2006	64	154	11	188	12	177	9	212
2007	30	159	16	171	14	178	11	250
2008	29	149	13	200	18	191	12	243
2009	21	142						
2010	67	156	21	179	40	197	8	253
2011	57	169	38	187	12	209	14	213
2013	85	172	37	204	37	204	22	252
average		160		189		196		238

Extrapolating the On-Farm Network fertilization data to the entire period of record available for crop yield data (1999-2013) showed a 24.3% increase in total fertilizer N applied in the watershed, and a 12.5% increase in total N inputs (fertilizer+deposition+biological fixation). Export of grain-N actually declined slightly (-2%) with the expansion of corn area, as lower-N-content corn replaced higher-N-content soybean. Even though the total mass of harvested corn greatly exceeds that for soybean, the amount of total N exported in soybean exceeds that for corn for every year of the record, due to the higher N content of soybean seeds.

Nitrogen returned to the soil from soybean residue declined but this amount was more than compensated by an increase from corn residue (figure 5). Overall, N returned to the soil from crop residue increased approximately 5% over the period of record (Table 2).

Discussion

Raccoon River watershed nitrate and climate

RRWS monitoring from 1999 to 2014 indicates a clear link between rainfall and NO_3-N. Nitrate concentrations and loads were lowest during dry years and were highest in the wet year of 2013 that followed the drought of 2012. Several studies have observed similar elevated NO_3-N following drought. For example Hagebro et al. (1983) stated that accumulation of NO_3-N may occur in agricultural soils because of reduced NO_3-N movement and transport during dry weather regimes. Schilling and Zhang (2004) found that maximum Raccoon River NO_3-N loads often occurred following the second year of below normal precipitation and discharge.

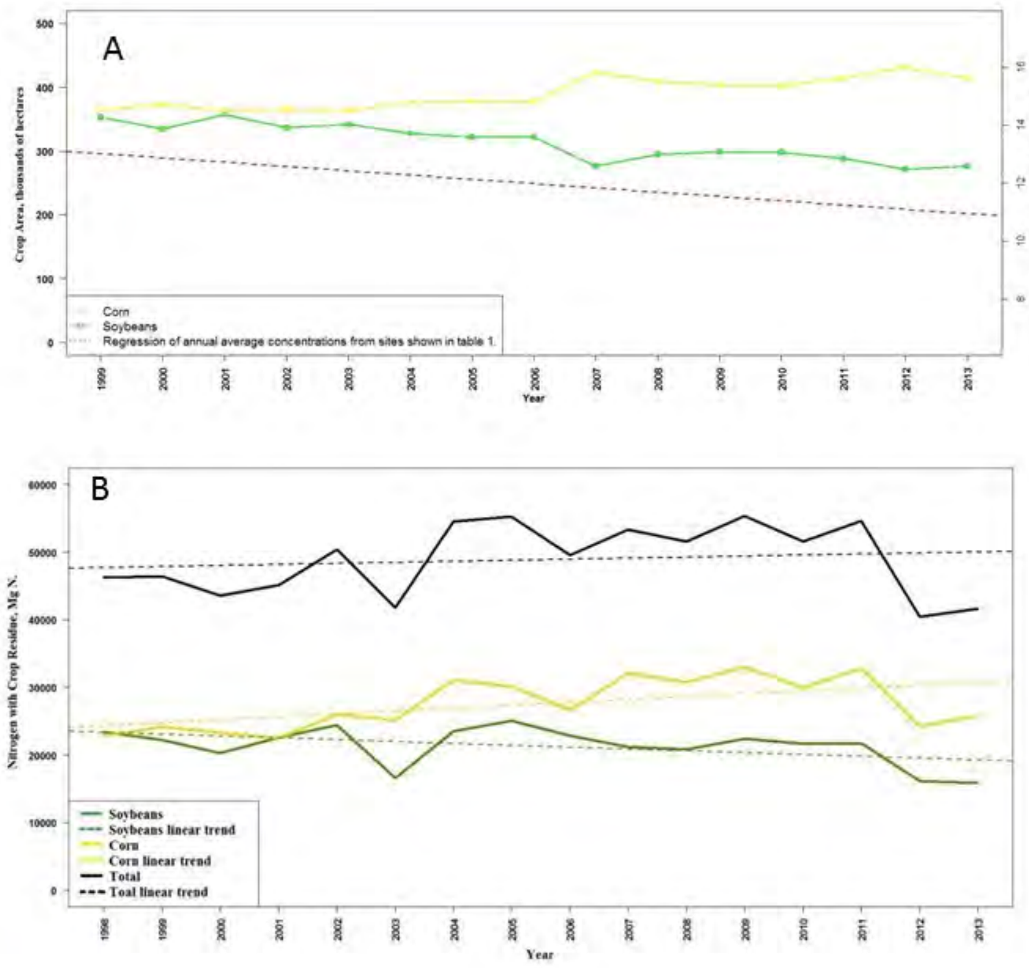

Figure 4: A) Crop area in the RRWS, 1999-2013, and linear trend of annual average NO3-N concentrations from sites shown in Table 1. B) Nitrogen returned to soils from crop residues, including linear trends, in the RRWS, 1999-2013.

Examination of DMWW and ACWA data here supports the idea of large NO_3-N transport following drought. The drought year of 2012 was the hottest recorded in the RRWS while precipitation was much below normal. This was followed by record rainfall across Iowa during April-May, 2013 (Hillaker 2013), and a record high NO_3-N concentration of 24 mg L^{-1} (ppm) was reported at DMWW in May 2013 (Beeman 2013).

It is noteworthy that this extra N left behind because of drought-repressed crop yields is much larger than the annual river NO3-N load, even in a wet year (2010, for ex.—Table 3). This illustrates the vulnerability of streams in the Mississippi River Basin to climate-induced perturbations of NO_3-N transport, and especially the Raccoon. Most of the RRWS lies in Prairie Pothole Region of central North America which has one of the most extreme and dynamic climates on Earth (Ahrens 2007). Preventing NO_3-N loss in a system that, by design, is saturated with N (Blesh and Drinkwater 2013) and that lies within an area of extreme and unpredictable weather clearly presents serious challenges.

While the April-July NO_3-N loading data presented here were highly correlated with April-July precipitation (correlation coefficients -0.70 to +0.79 for all five flow-gauged ACWA sites), loads were not correlated with the estimates of the simplified N balance or with N inputs from the previous or same year. It would seem reasonable to expect the magnitude of the N balance would be manifested in the April-July

NO_3-N loads/concentrations the following year, as the N balance would be an indicator of the surplus (or deficit) at the end of the growing season. The January-December river NO_3-N loads at the DMWW site near the mouth of the Raccoon River do not correlate well with any variable in the N budget. We concur with other studies (Schilling and Lutz 2004; Basu et al. 2010) that demonstrated precipitation and discharge drive river NO_3-N export.

Decreasing nitrate in the Raccoon River watershed

Although climate and discharge largely influence river NO_3-N export in any given year, NO_3-N levels decreased during the 1999-2014 period. At first glance one might have expected that river NO_3-N levels should have increased, given that inputs of fertilizer N increased 24% with the expansion of corn area while grain N actually declined 2%, as harvest of higher-N soybean seed was replaced by lower-N corn grain. However, neither NO_3-N concentrations nor loads correlate with N inputs either alone or as a covariate with precipitation. Furthermore, wet weather patterns during the past 16 years should have favored NO_3-N export (Basu et al. 2010).

The fact that RRWS NO_3-N did not increase suggests improved crop management may be having some incremental effects on water quality. Management has become increasingly sophisticated in recent years, and practices related to cover crops, tillage, weed and pest control, drainage, and integrated nutrient use may be increasing nitrogen use efficiency (Balasubramanian, et al. 2004) and improving water quality. But linking incremental water quality improvements to crop and land management can be agonizingly difficult (Schilling et al. 2013).

Table 3. Simplified N budget for the RRWS.

Year	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Total N applied Corn (Mg)	69,541	71,346	69,436	69,524	69,754	72,611	73,746	73,582	84,352	82,940	80,962	80,516	83,377	87,695	84,551
N applied to Soybean (Mg)	5,529	5,398	5,591	5,274	5,360	5,139	5,051	5,042	4,336	4,623	4,688	4,673	4,517	4,258	4,334
Soybean N Fixation from Previous Year (Mg)	52,784	47,798	43,557	47,030	54,274	43,796	55,332	59,842	54,406	51,499	46,214	53,789	50,648	51,293	35,636
Atmospheric Deposition (Mg)	19,428	14,194	18,587	17,637	18,075	21,484	19,490	19,250	28,187	26,519	21,709	27,699	18,039	13,671	17,179
Total N Inputs (Mg)	147,282	138,736	137,173	139,466	147,463	143,029	153,620	157,716	171,281	165,580	153,573	166,676	156,580	156,917	141,699
N exported in Corn Grain (Mg)	34,548	33,397	32,207	37,182	36,064	44,461	43,219	38,165	45,962	44,185	47,258	42,984	47,168	34,707	36,987
N exported in Soybean Grain (Mg)	56,418	51,345	57,350	61,993	42,257	59,684	63,789	58,002	53,826	52,938	56,779	55,171	55,171	41,002	40,195
River N Load (minus point sources) Jan-Dec (Mg)	28,519	-711	14,944	10,036	14,576	17,230	11,172	7,509	29,607	24,429	14,797	29,874	11,296	415	23,921
Total N Outputs (Mg)	119,486	84,031	104,501	109,210	92,897	121,376	118,181	103,677	129,395	121,552	118,834	128,029	113,635	76,124	101,103
N Balance (Inputs-Outputs) (Mg)	27,796	54,704	32,671	30,256	54,566	21,653	35,439	54,039	41,886	44,029	34,738	38,648	42,945	80,793	40,596
N from previous year's crop residue (Mg)	46,272	46,393	43,588	45,087	50,402	41,836	54,548	55,265	49,504	53,282	51,603	55,320	51,603	54,570	40,423
N use efficiency for corn (grain N/fertilizer N)	0.50	0.47	0.46	0.53	0.52	0.61	0.59	0.52	0.54	0.53	0.58	0.53	0.57	0.40	0.44

Changes in crop rotations as a contributing factor in decreasing nitrate

Total cropped area in the watershed declined 2.5% during the study period. Corn area increased 19%, but soybean area, which typically receives small or no inputs of N in Iowa, declined 24% throughout a period of diminishing river NO_3-N (figure 3). We suggest that management decisions related to the cultivation of soybeans may disproportionately affect river NO3-N (compared to corn management), and fewer soybean acres may have contributed to its decline in the RRWS.

Microorganisms respond quickly to additions of easily-decomposed organic matter (Sarrantino and Scott 1988), and soybean residue produces mineralization rates about 1.5 times greater than non-legumes (Burkart et al. 2005). Incorporation of soybean residue with a lower C:N ratio than corn residue can affect the carbon-nitrogen cycle (Blackmer and Green 1995) and rapidly mineralize soil organic N to NO_3-N following tillage, especially when there is no possibility of plant uptake (Drinkwater et al. 2000), as is the case in Iowa following harvest.

Nitrate resulting from incorporation of soybean residues would be immediately vulnerable to leaching and would remain so as long as the ground is unfrozen to the depth of the tile drainage. It seems likely that a reduction in soybean area that is tilled following harvest, whether by adoption of more C-C rotations or reduced tillage management practices, could reduce NO_3-N resulting from soil mineralization and subsequent leaching. It is important to note here the distinction between this NO_3-N and fall applied fertilizer N, which is usually applied in the form of anhydrous ammonia and initially present in the soil as ammonium-N (NH_{4+}). Ammonium-N is much less vulnerable to leaching if applied when autumn soil temperatures are less than 50F (Randall et al. 2003).

Synchronizing N from mineralization with crop needs is crucial to reconciling yield optimization with NO_3-N export in annual cropping systems (Drinkwater et al. 2000). Mineralized soil organic N is the major source of this nutrient, even when fertilizer inputs of N are present (Stevens et al. 2005; Gardner and Drinkwater 2009). The large majority of N present in Iowa soils resides in organic compounds embedded within the soil organic matter (Christianson et al. 2012). We believe a possible reason more C-C in the RRWS has not increased NO_3-N flux is that less area is being devoted to soybean cultivation that requires more thoughtful management for mineralization and the associated biological processes.

When considering soil organic matter, it is important to recognize that soybean produces less crop residues than corn. Increased corn area in the RRWS (i.e. more C-C vs SB-C) increased residue N returned to watershed soils about 5% (Table 3), increasing soil organic matter stocks and likely affecting soil N balances. Sawyer et al. (2006) reported measured soil C and N balances <0 for SB-C, but >0 in C-C at four Iowa sites when economically optimum N rates were applied. Soil organic N increased as much as 20 lb/ac-yr in some of the soil samples collected from the C-C systems. Thus when we contrast SB-C vs C-C, the soybean phase of SB-C presents a scenario favoring mineralization of soil organic N stocks into leachable NO3-N, while both phases of the C-C rotation favor incorporation of fertilizer N into increased stocks of soil organic N. Increases of N returned to RRWS soils by crop residues (table 4) associated with more corn and less soybean area is consistent with Sawyer et al. (2006) and reduced N transport resulting from mineralized soil organic matter.

Less denitrification occurring under soybean than under corn may effectively make more NO_3-N available for loss. In the context of our N budget, unaccounted-for N averages 28% of inputs for 1999-2013. In this simplified N budget, the major loss pathways for this unmeasured N are denitrification and volatilization. David et al. (2009) evaluated six different watershed models for the neighboring state of Illinois and each predicted lower denitrification fluxes for soybean, with an average difference of -29% compared to corn. Christianson et al. (2012) reported denitrification in Iowa 8.6 to 9.9 lb/ac in continuous corn but only 5.9 to 7.1 lb/ac in corn following soybean and 0.7 lb/ac for soybean. Larger corn area likely means a greater amount of NO_3-N lost to denitrification, and less available for loss through the drainage network. Also, the period of 2007-2010 and 2013 was very wet with soil conditions favorable for denitrification. Thus, saturated soils in these years surely contributed to additional denitrification independent of the relative areas planted in corn and soybean.

Finally, drainage water through tiled plots tends to be a higher percentage of total precipitation received in soybean than corn (Weed and Kanwar, 1996; Kaspar et al. 2012), largely because of differences in evapotranspiration. Since tile systems are the major NO_3-N loss pathway (Schilling and Zhang 2004), the elevated tile water discharge during soybean years may increase NO_3-N export. Helmers et al. (2011), working on test plots of 9.1 ac only 11 miles from the RRWS, showed average annual NO_3-N loss 8.9 lb/ac higher from SB-C than C-C over 4 years when corn N rates to each were 150 and 199 lb/ac-yr, respectively. As NO_3-N concentrations were similar or somewhat higher under corn, the higher NO_3-N yields under soybean were due to greater drainage volumes under soybean.

Limiting nitrate loss

Reducing nutrient export to streams in the Mississippi River Basin has often focused on managing N inputs for corn production. We believe our analysis, however, indicates that improving SB-C management practices may have larger positive effects on riverine NO_3-N export than solely focusing on fertilizer N inputs for corn. Fertilizer N comprises <50% of the N inputs in the RRWS (Table 4). Developing management strategies that minimize tillage following soybean harvest and preventing loss of soil organic carbon and N in SB-C may have more potential to reduce NO_3-N export in the RRWS than refinement of N fertilization strategies for corn.

It is true that small drainage studies (Randall and Goss, 2001; Brouder et al. 2005) show increased NO_3-N leaching when N rates applied to corn exceed optimal rates, implying wise management of fertilizer inputs will improve water quality. That said, data presented here confirms precipitation and discharge are driving inter-annual variability in export of NO_3-N at the watershed scale. Modest shifts in production management, which may include modifying the ratio of corn:soybean area and implementing best management practices that focus on reducing the supply of N on the landscape, are not likely in the near term to overcome the phenomenon of precipitation- and discharge-driven NO_3-N loss at the watershed scale.

Conclusions

Despite warnings of increased river NO_3-N from more C-C rotations fueled by ethanol demands, increased corn area and fertilizer inputs in the RRWS did not increase river NO_3-N. Since 1999, NO_3-N concentrations appear to be declining at the vast majority of RRWS sites, although the ratio of river NO_3-N load to applied fertilizer N has changed little since 1990. Water quality following the 2012 drought demonstrates how exposed this system is to extreme climatic perturbations, common in this area of North America.

Our study suggests the decreasing NO_3-N concentrations may be related to decreasing soybean cultivation in the watershed. Less area in soybean may have indirectly reduced NO_3-N transport by shrinking land area most vulnerable to NO_3-N export, increasing denitrification in the soil profile, and decreasing water throughput in tiled fields. This suggests better management of this crop will improve water quality.

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